Research Opportunities in Macromolecular Complex Systems

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Scientific and Operational Leaders

DOE Office of Science, Lehman Review
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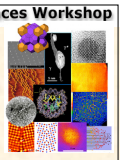
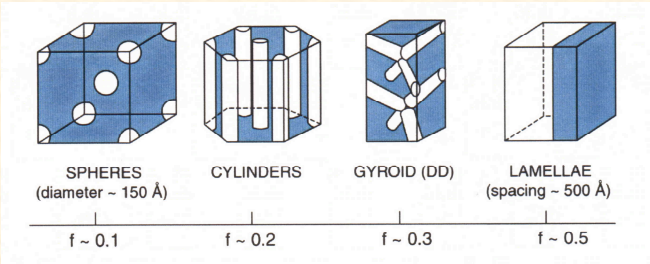
CNMS Planning Workshops

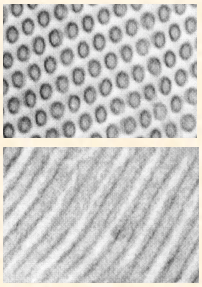
Synthetic and Bio-Inspired Macromolecular Materials



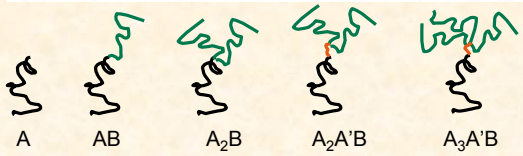
- Scientific Grand Challenges
  - To design and control the nanoscale organization of macromolecular materials to achieve novel functionality
- Key Issues
  - Design and synthesize complex macromolecular architectures
  - Develop directed self-assembly strategies
  - Generate biological function by hierarchical structures to achieve material properties
  - Understand the effect of nanoscale confinement on structure, dynamics, and properties of macromolecular systems
  - Understand and control the nature of interfaces in nanophase macromolecular systems
  - Develop a theoretical understanding and predictive capabilities to achieve the above

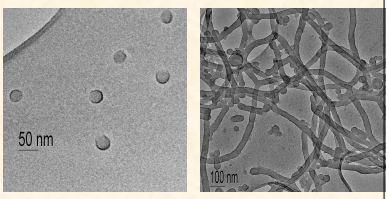
Diblock Polymer Morphologies





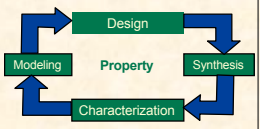
TEM of Poly(styrene-*b*-1,3-cyclohexadiene)





TEM of poly(acrylic acid)-*b* polystyrene

Enabling Nanoscience Tools at CNMS



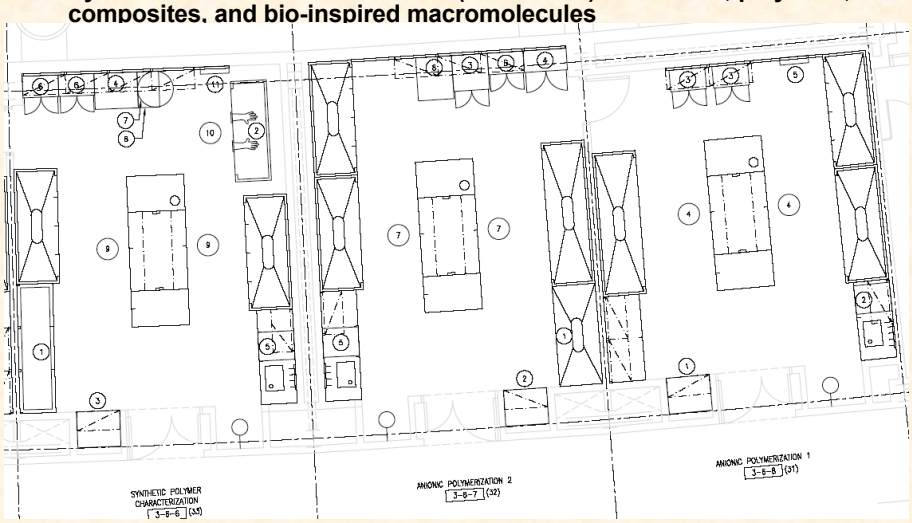
- **Synthetic toolbox for construction of well-defined macromolecular materials**
  - **Anionic and controlled radical polymerization methods**
  - **Develop new approaches for design and synthesis of novel polymer architectures and hybrid materials**
- **Characterization tools for macromolecular materials**
  - **State-of-the-art characterization tools**
  - **Neutron scattering tools**
    - **SANS - shape, structure, location, and evolution**
    - **Reflectometry - molecular scale structure at interfaces**
    - **H/D contrast- imaging components on nm length scales**
      - **Need for well-defined deuterated monomers and polymers**
- **Provide an understanding of how to control polymer structure and how structure relates to property**

Need for Deuterated Materials

- NSF Workshop on Neutron Scattering for Chemistry and Chemistry/ Biology Interface, and NSF Workshop on Sample Environments for Neutron Scattering Experiments, September 23-26, 2003
  - "Providing users with the tools and facilities needed to produce deuterated materials would enhance both the quality and quantity of neutron experiments that can be done at SNS and other neutron research centers, and would make feasible new and more sophisticated experiments than can be presently performed."
- Recommendations:
  - "A top priority (is)…sample preparation laboratories, including deuteration facilities, convenient to the beam line."
  - "Create a general deuteration/isotope materials facility for the production of deuterated and novel isotopically substituted materials..."
  - "Develop methods for the synthesis of labeled polymers, peptides, surfactants, and other complex biomolecules and other small molecules of interest."
- **CNMS is uniquely posed to address many of the deuteration needs of the scientific community**

Facilities

- Seven synthetic and three characterization labs
  - Synthesis and characterization of (deuterated) monomers, polymers, composites, and bio-inspired macromolecules



Polymer Characterization Tools

- Molecular weight characterization
  - Gel Permeation Chromatography (GPC) with refractive index, light scattering, viscosity, and UV-Vis detection
    - Capabilities for aqueous and nonaqueous GPC
  - High temperature GPC (≥150 °C) with refractive index, light scattering, and viscosity detector
  - MALDI-TOF-MS
  - *Solution and solid-state 700 MHz NMR*
    - Determine tacticity (configuration) of polymer chain, monomer sequencing in copolymers, solution structure, solid-state morphology, polymer environments, monomer characterization
  - Static and dynamic light scattering
    - Conformation, shape, size and size distribution of polymers as a function of temperature, solvent, pH, salt concentration, etc.
  - Membrane osmometry

Polymer Characterization Tools

- Thermal and mechanical properties
  - Differential scanning calorimeter (DSC)
    - Phase transitions (*Tg*, and T_m) in polymers
  - *Thermal gravimetric analyzer (TGA)*
    - Thermal and oxidative stability of polymers, composites, and carbon nanotubes
  - *Dynamic Mechanical Analysis (DMA)*
    - Elastic and storage modulus of a sample as a function of temperature, time and frequency of an oscillating load

Polymer Characterization Tools

- Spectroscopic Characterization
  - Fourier transform infrared (FTIR)
    - Functional groups and structure
    - Polymer surfaces by ATR and photoacoustic spectroscopy
  - Ellipsometer
    - Polymer surfaces
  - Ultraviolet-Visible-Near Infrared (UV-Vis-NIR)
    - Chromophores, end groups, and electronic properties
  - *Fluorescence Spectrometer*
    - Electronic properties of polymers (and carbon nanotubes), polymer motion, polymer compatibility, polymer structure, etc.
  - *Gas Chromatography-Mass Spectrometry*
    - Characterization of monomers and deuterated monomers

Polymer Characterization Tools

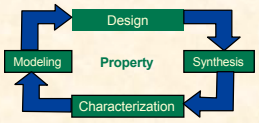
- Other resources at the CNMS
  - Computational tools (Nanomaterials Theory Institute)
  - Nanofabrication Research Labs
  - AFM and TEM imaging of macromolecular materials
  - Raman Spectrometer
- Other resources ORNL/UT
  - Neutron scattering (HFIR and SNS)
  - Small angle X-ray scattering
  - Rheology tools

Current Technical Resources

- Jimmy Mays - UT/ORNL Distinguished Scientist
  - Scientific leader - Anionic polymer synthesis and characterization
- Phillip Britt - Senior Research Staff ORNL
  - Operational and scientific leader - polymer characterization and controlled radical polymerization
- Kunlun Hong - New Staff (Strategic hire, July 6, 2004)
  - Polymer synthesis (anionic and controlled radical), monomer synthesis, and characterization (GPC, NMR, and light scattering)
- David Uhrig - Postdoctoral Research Associate
  - Anionic polymer synthesis, monomer synthesis, and silane coupling chemistry
- Joseph Pickel - Postdoctoral Research Associate
  - Characterization of polymers (aqueous and non aqueous GPC with light scattering, MALDI-TOF-MS, TGA, and DSC) and polymer synthesis (anionic and controlled radical)

Unique Capabilities at CNMS for World Class Research in Macromolecular Science

- "One Stop Shopping" for all of your polymer needs: design, synthesis, characterization, deuteration, and TMS



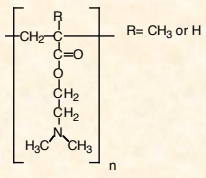
- Unique synthetic techniques for the preparation of complex polymer architectures (such as stars, combs, and hyperbranched polymers) that are only available in a few groups in the world
- Unique capabilities for preparing and characterizing polymer-carbon nanotube composites
- Emerging synthetic capabilities in preparation of novel polymer architectures based solely or in part on amino acids

CNMS Users

- Call for Jump Start User-Initiated Nanoscience Research Program - July 22, 2003
  - Received 71 proposals
    - 38 proposals involved Macromolecular Complex Systems research focus theme
  - Only 13 (34%) proposals accepted
    - 6 proposals on block copolymers synthesis by anionic methods
      - 3 for deuterated polymers - neutron scattering studies
    - 7 proposals focused on characterization of materials
  - Users from
    - University of Massachusetts (3), Clemson, University of Alabama Tuscaloosa, Virginia Tech, Northwestern University, University of Tennessee, North Carolina State University, Institute of Polymer Research Dresden (Germany), Luna Innovations Inc., and ORNL (2)

Topology Effects on Cationic Polymers as Gene Transfer Agents

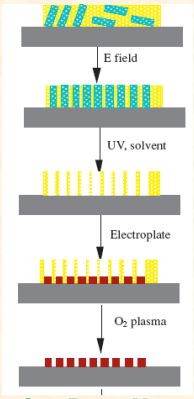
- Tim Long and Amanda Rudisin (undergraduate)
  - Virginia Polytechnic Institute and State University
- Cationic polymers, such as poly(2-dimethylamino)ethyl methacrylate (PDMAEMA), electrostatically bind to plasmid DNA
- Cationic polymers are capable of transfecting plasmid DNA into cells
- Goal: Determine effect polymer topology and molecular weight on transfection efficiency
- Approach: Aqueous GPC light scattering
- Linear PDMAEMA
- Branched PDMAEMA-co-poly(ethylene glycol dimethacrylate)
- Linear PDMAEA



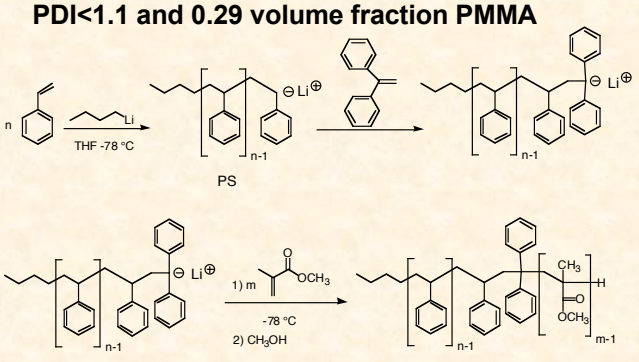
Magnetic Nanowires Arrays using Self-Assembling Polymers

- **Martin Bakker and Vishal Warke (graduate student)**

  Center for Materials for Information Technology, University of Alabama
- **Goal: Prepare highly oriented magnetic nanoparticles with a narrow size distribution for high density hard drive applications using a poly(styrene)-*block*-poly(methyl methacrylate) copolymer, which forms a hexagonal array of PMMA cylinders in a continuous PS matrix**

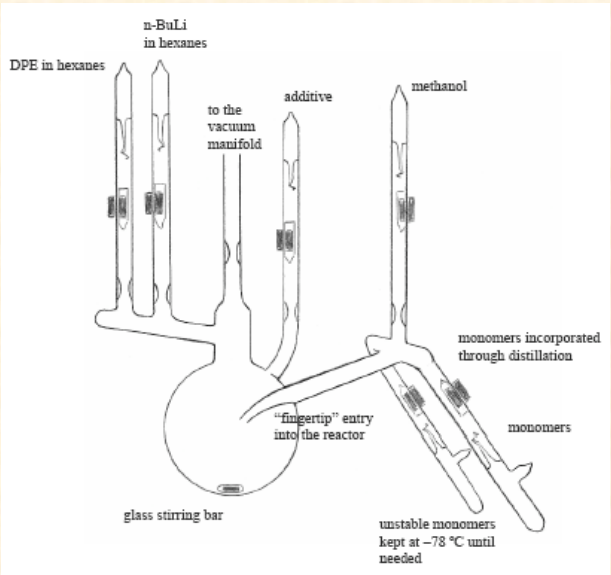


– **Approach: Prepare PS-*b*-PMMA with M_w = 39K and PDI<1.1 and 0.29 volume fraction PMMA**

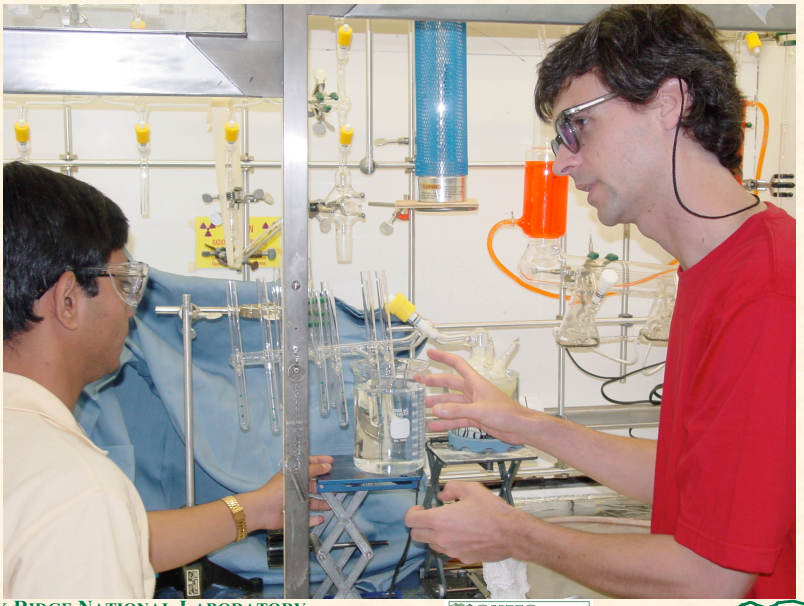


M_w = 41 K
PDI = 1.1

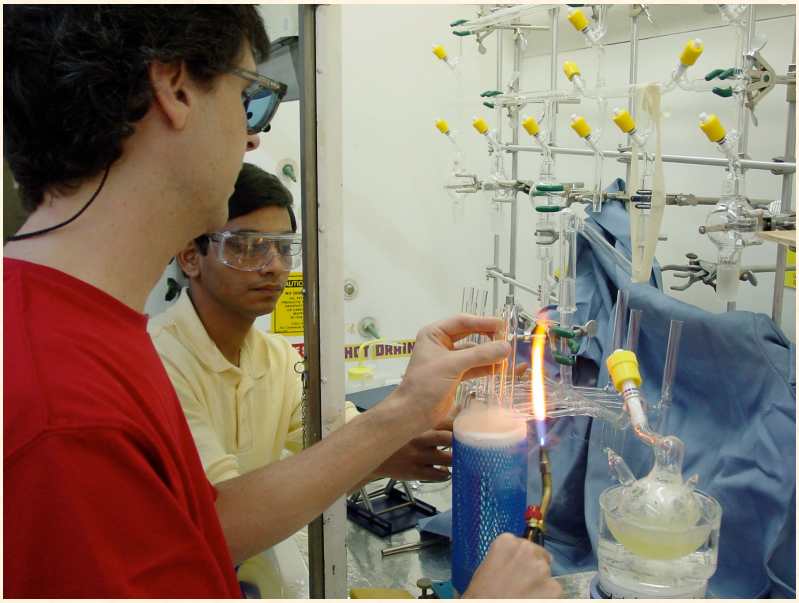
Vessel for Block Copolymer Synthesis



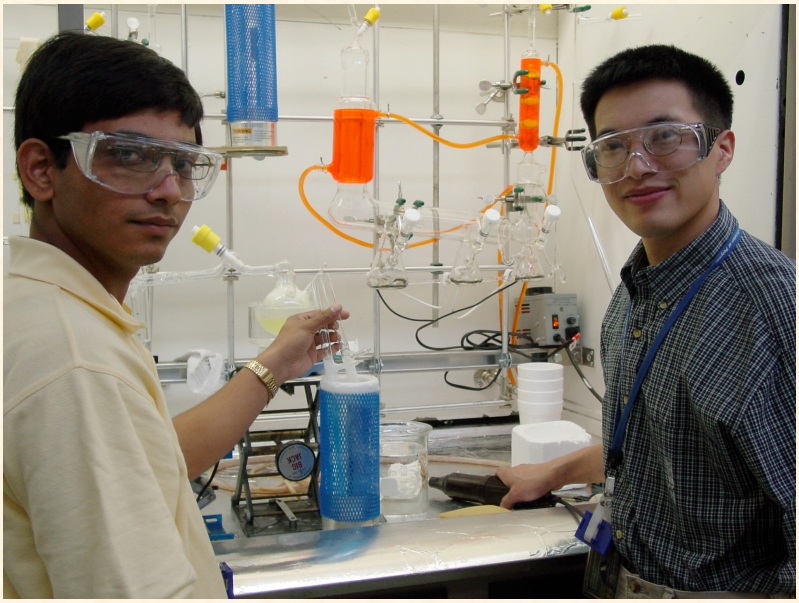
David Uhrig and Vishal Warke



Sealing Ampules of Purified Monomer

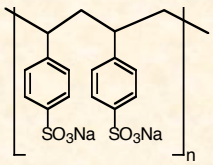


Vishal Warke and Kunlun Hong

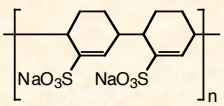


Synthesis and Characterization of Polyelectrolytes

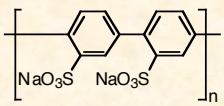
- Mike Simonson, Oak Ridge National Laboratory
- Systematic investigation of the nanoscale structures formed by polyelectrolytes in solution
- Goal: Investigate the effect of chain stiffness on polyelectrolyte conformation and counterion interactions in solution by neutron, X-ray, and light scattering techniques
- Approach: Synthesis of a series of polymers and deuterated polymers (of similar DP) with different backbone stiffnesses:
  - Poly(styrene sulfonate) - flexible (PSS)
  - Poly(1,3-cyclohexadiene sulfonate) - semiflexible (PCHDS)
  - Poly(1,4-phenylene sulfonate) - rigid rodlike (PPS)



PSS

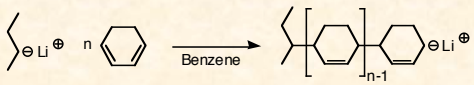


PCHDS



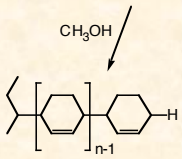
PSS

Synthesis of Poly(1,3-Cyclohexadiene)

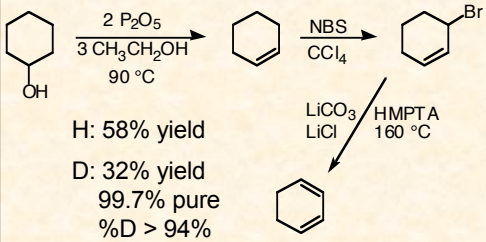


H: M_n = 7.8 K
PDI = 1.07

D: M_n = 8.7 K
PDI = 1.06

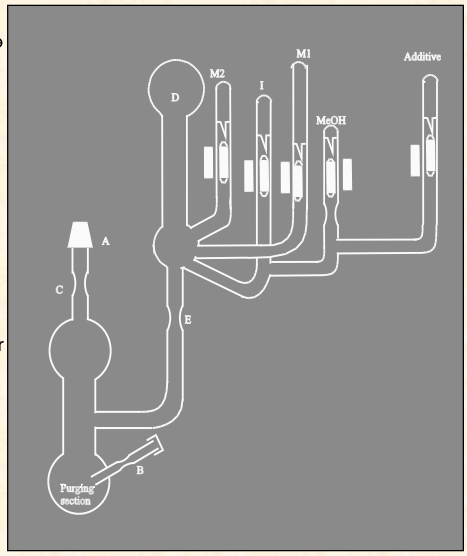


Synthesis of deuterated monomer



H: 58% yield

D: 32% yield
99.7% pure
%D > 94%



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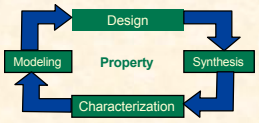

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